Journal of Forestry Research (2013) 24(4): 741−746
DOI 10.1007/s11676-013-0413-2

ORIGINAL PAPER

Improvement of wood properties by composite of diatomite and "phenol-melamine-formaldehyde" co-condensed resin

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Received: 2012-02-28; Accepted: 2012-05-07
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Abstract: We improved the overall performance of fast-growing poplar by utilizing a low-cost, effective and simple method. The fast-growing poplar was modified by a vacuum-pressure impregnation method with three types of modification solutions composed of phenol-melamine-formaldehyde (PMF) co-condensed resin, diatomite, and 3-aminopropyl (diethoxy) methylsilane. We measured the weight percent gain (WPG), bulking, leaching, anti-swelling efficiency (ASE), water-repellent effectiveness (WRE), and oxygen index of the modified specimens. All of the wood physical properties, which are beneficial for human uses, were significantly improved by the treatment. We improved various characteristics of wood and the oxygen index of poplar above 48.6% after the modification using diatomite and PMF co-condensed resin.

Keywords: wood modification; phenol-melamine-formaldehyde co-condensed resin; artificial fast-growing poplar; diatomite

Fund project: This research was supported by Program for New Century Excellent Talents in University (NCET-10-0311), the National Natural Science Foundation of China (31000271) and the Fundamental Research Funds for the Central Universities (DL11BB29)

The online version is available at http://www.springerlink.com

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Corresponding editor: Yu Lei

Introduction

Fast-growing poplar has a number of advantages such as rapid growth and short cultivation time. However, its shortcomings include low density, poor size stability and low surface hardness. To exploit the advantages of this fast-growing species, many attempts were made to enhance the properties of poplar wood, including chemical modification by small organic molecules, formation of wood/polymer composite by the impregnation of solid wood with water-soluble, thermosetting resin systems, organic vinyl monomers in the presence of a cross-linking agent followed by in situ polymerization (Cai et al. 2010; Devi and Maji 2008), and formation of micro- and nanomodified wood/polymer composite by intercalating micro- and nanomaterial and polymers into the wood.

Based on its outstanding effect on the overall improvement of wood performance, the field of composite wood has attracted researchers from every region of the world. The preparation of wood-based inorganic composites by sol-gel processes yielded comparatively high dimensional stability and flame resistance (Ogiso and Saka 1994; Saka and Tanno 1996). Devi and Maji (2012) reported a type of modified wood with styrene-acrylonitrile copolymer and organically treated nanoclay. Yu (2011) and co-workers compounded poplar wood with MMT to improve the wood for new functions and uses. Sodium silicate has been used as the main reagent to modify wood, resulting in improved flame resistance, decay resistance and dimensional stability (Takeshi and Tohru 1993; Takeshi et al. 1991; Takeshi et al. 1992). Li and Wang (2010) manufactured a wood/calcium carbonate compound material in situ using the method of bionic mineralization, which is hydrophobic and oleophobic.

Phenol-melamine-formaldehyde (PMF) co-condensed resin with lower curing temperature and shorter curing time was first researched and created to replace the phenol aldehyde resin (Gu 1999). PMF co-condensed resin has been improved, and pos-

sesses more virtues, such as waterproof property, long storage period, low concentration of free phenol and aldehyde, environmentally friendly performance, retaining the natural color of the wood and low cost. Diatomite ($SiO_2 \cdot nH_2O$) is a pale, soft, lightweight sedimentary rock, which has many advantages, including large specific surface area, high absorption capacity, low density, high melting-point, chemical inertness, small grain size, low thermal conductivity and low price (Al-Degs et al. 2001; Şan et al. 2009). In the present study, we used diatomite and PMF co-condensed resin because of their advantageous characteristics as wood treatments. We successfully modified fast-growing poplar using a vacuum-pressure impregnation method with PMF co-condensed resin, diatomite, and 3-aminopropyl (diethoxy) methylsilane. We measured the effects on various physical, mechanical and thermal properties of wood/diatomite/PMF co-condensed resin composite. The overall performance of fast-growing poplar wood after treatment was significantly improved, and our research employing diatomite to improve the properties of wood is unprecedented.

Materials and methods

Sample preparation

Poplar wood was collected locally, and diatomite was obtained from Jilin, China. Sodium hydroxide (96%) was obtained from Tianjin Kaitong Chemical Reagent Co., Ltd. Phenol (analytically pure) was purchased from Tianjin Yongda Chemical Regent Development Center. Formaldehyde (analytically pure) was obtained from Dandong Longhai Reagent Factory. Melamine (99.5%) was purchased from Shanghai Shanpu Chemical Co., Ltd. 3-Aminopropyl (diethoxy) methylsilane (97%) was obtained from Aladdin Chemistry Co., Ltd. All of the above chemicals were used as received without further purification.

Poplar wood was cut into 26.5 mm × 27.5 mm × 5 mm and 2 mm × 6.5 mm × 150 mm (radial × tangential × longitudinal) samples to test dimensional stability, water uptake, bulking, leaching and antiflaming. Before modification, the wood samples were immersed in distilled water until their weights reached the maximums, and then, the samples were completely dried in an oven at 103±5°C until constant weights were obtained. The dimensions and weights of samples were measured after both of these steps.

Preparation of phenol-melamine-formaldehyde (PMF) co-condensed resin

First, the melting phenol (P) and formaldehyde (F) were mixed in the reaction kettle by launching blender. Then the reaction kettle was heated, and the melamine was added in the reactant. During the whole reaction, the pH of the mixture was adjusted by adding lye (NaOH). In the process of heat preservation, the turbidity of the product was measured till the globular object appeared in it. Finally, the PMF co-condensed resin, which is a type of rice yellow transparent liquid, was obtained.

The optimal content of diatomite dispersed into the resin

PMF co-condensed resin and diatomite were mixed at ratios of 100:0.1, 100:0.15, 100:0.2, 100:0.25 and 100:0.3 by 10 min ultrasound treatment at ambient temperature. The mixtures were then left to stand for about 12 h at ambient temperature. Diatomite in the mixtures at ratios of 100:0.25 and 100:0.3 sunk to the bottom of the beakers. Therefore, the optimal content of diatomite dispersed into the resin was 0.2%.

Formation of PMF co-condensed resin /diatomite (PMFD) composites

PMFD composites were prepared by two methods, PMFD1 and PMFD2. PMFD1 and PMFD2 were composed by compounding PMF co-condensed resin and unmodified diatomite, and PMF co-condensed resin and modified diatomite at a ratio of 100:0.2 by 10 min ultrasound treatment at room temperature, respectively. Modified diatomite was obtained by using 35% of silane coupling agent of 3-aminopropyl (diethoxy) methylsilane.

Preparation of wood/PMF, wood/PMFD1 and wood/PMFD2 composites

Based on the exploratory experiment, the dried poplar wood samples were placed into an impregnation tank with PMF, PMFD1 or PMFD2 intercalation solution under a vacuum degree of -0.08 MPa for 0.5 h. Normal pressure was then restored for 0.5 h, after which pressure of 0.8 MPa for 12 h was applied. After the high pressure, the wood products were removed from the tank and dried in an oven at 103±5°C, and then specimen 1 (wood/PMF composites), specimen 2 (wood/PMFD1 composites) and specimen 3 (wood/PMFD2 composites) were obtained. The surface microstructure of original diatomite and specimen 3 were analyzed by scanning electron microscopy (SEM). In addition, wood samples measuring 26.5 mm × 27.5 mm × 5 mm (radial × tangential × longitudinal) after treatment were placed into distilled water for 24 hours at ambient temperature, and then dried in an oven at 103±5 °C for 24 h. Their dimensions and weights were measured after each step.

Determination of wood properties

Characteristics of WPG, bulking and leaching effect, dimensional stability and water uptake were quantified by measuring three replicate poplar wood samples (26.5 mm × 27.5 mm × 5 mm).

Weight percent gain (WPG)

WPG after resin loading was calculated according to the formula:

$$WPG = \frac{m_2 - m_1}{m_1} \times 100\% \quad (1)$$

where, m_1 and m_2 are the oven dry weights of wood blocks before

and after resin treatment.

Anti-swelling efficiency (ASE)
ASE due to impregnation was calculated according to the formula:

$$ASE = \frac{S_0 - S}{S_0} \times 100\% \quad (2)$$

$$S_0 = \frac{V - V_0}{V_0} \times 100\%$$

$$S = \frac{V_3 - V_2}{V_2} \times 100\%$$

where, V and V_3 are the volumes of wood blocks before and after treatment, V_0 and V_2 are the oven-dry volumes of wood blocks before and after treatment.

Bulking effect (B)
B due to impregnation was calculated as follows:

$$B = \frac{V_2 - V_1}{V_1} \times 100\% \quad (3)$$

where, V_1 is the oven-dry volume of the untreated wood.

Leaching effect (L)
L after resin loading was calculated according to the formula:

$$L = \frac{m_2 - m_4}{m_2 - m_1} \times 100\% \quad (4)$$

where, m_4 represents the oven-dry weight of the treated wood.

Water-repellent effectiveness (WRE)
WRE after resin loading was calculated as follows:

$$WRE = \frac{G_0 - G}{G_0} \times 100\% \quad (5)$$

$$G_0 = \frac{m - m_0}{m_0} \times 100\%$$

$$G = \frac{m_3 - m_2}{m_2} \times 100\%$$

where, m is the weight of untreated blocks, m_0 is the oven-dry weight of untreated wood blocks, and m_3 is the weight of treated blocks.

Antiflaming effect
A higher oxygen index indicates better antiflaming effect while a lower oxygen index indicates poorer antiflaming effect. Therefore, the antiflaming effect of samples was reflected by the oxygen index of wood specimens measuring 2 mm × 6.5 mm × 150 mm (radial × tangential × longitudinal), which was measured according to GB7911.6-87.

Results and discussion

Natural diatomite and PMF resin/modified diatomite composite

Natural diatomite frustules are mainly divided into two categories: centric (discoid) and pennate (elongate to filiform). As shown in Fig. 1a, the centric diatom used in this work had a radius of approximately 10 μm, while the length of pinnate shape was greater than 20 μm. Both categories of diatomite have a large void volume and highly porous structure (Khraisheh et al. 2004). Moreover, diatomite contains many siloxane groups or –Si–O–Si– bridges with oxygen atoms, and the surface is terminated by -OH groups and oxygen bridges (Khraisheh et al. 2005). These characteristics of diatomite make well suited to applications requiring sorbent and filling compounds. Consequently, in our study, the addition of diatomite can not only decrease the content of free formaldehyde and phenol in resin, but also improve the combination property with PMF co-condensed resin. Fig. 1b shows the SEM image of wood/PMFD2 composite surface. Compared with natural diatomite particles, only a tiny portion of modified diatomite particles were exposed to the ambient air, and the distribution of these tiny portions was uniform. This demonstrated that the modified diatomite particles were well dispersed by ultrasound treatment of resin at the ratio of 0.2:100, and the resin with modified diatomite particles was successfully and evenly attached to the wood surface. This indicates that the following procedures were feasible.

Increase in mass due to modification

WPGs of all specimens were greater than 150%, suggesting that the quality of all samples was significantly enhanced by the presence of PMF co-condensed resin. It also indicates that the addition of trace diatomite did not affect the quantity of resin injected into the wood (Fig. 2). Specimen 3 displayed an obviously higher WPG than specimen 2, while the latter possessed a slightly higher WPG than specimen 1, which reflects that the addition of diatomite increased the quality of specimen significantly, and the presence of the coupling agent slightly boosted this effect (Fig. 2). The reasons for these results are summarized as follows: (1) the PMF co-condensed resin and diatomite intercalated into the tracheids and cell cavities of wood after vacuum–pressure treatment, and (2) 3-aminopropyl (diethoxy) methylsilane interacted with the resin, diatomite, and wood through its bonds of Si-O and Si-R. However, the effect of diatomite and the coupling agent on increasing the quality of specimens was

limited, due mainly to the low concentration of diatomite (0.2%).

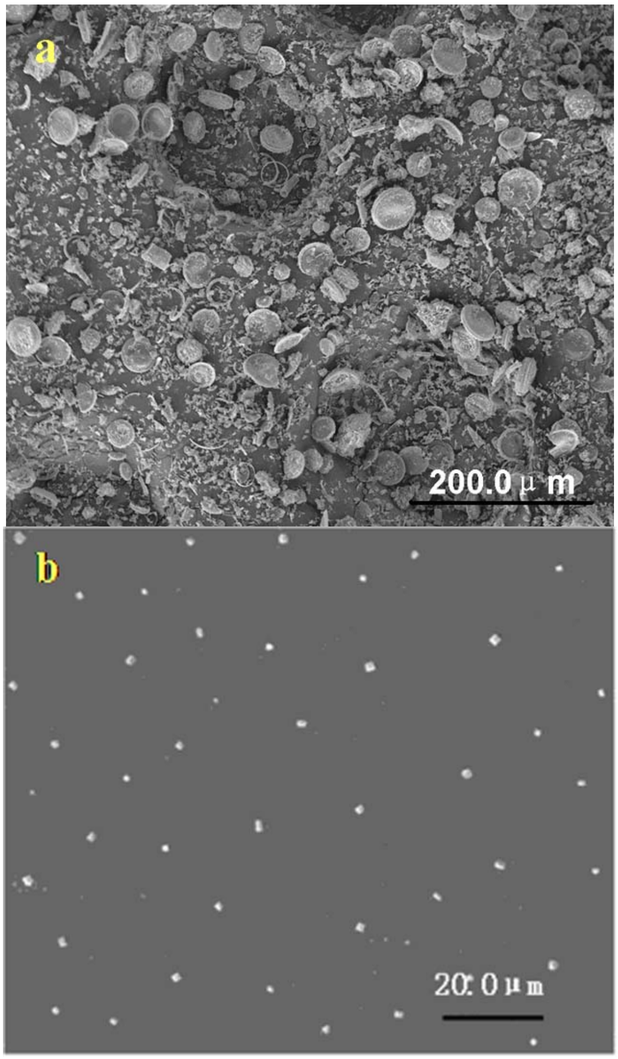

Fig. 1 SEM image of (a) original diatomite and (b) wood/PMF co-condensed resin/modified diatomite composite

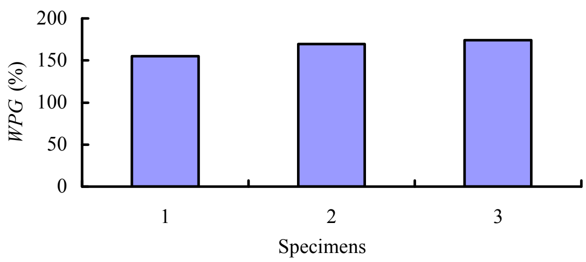

Fig. 2 WPG of poplar specimen due to the modification with (1) PMF, (2) PMFD1, or (3) PMFD2

Dimensional stability and bulking effect

Compared with untreated specimens (ASE=0), the dimensional stability of all specimens after treatment was significantly improved (Fig. 3a). This is because the "volume effect" plays an important role in the improvement of dimensional stability (Li et al. 2003). Many researchers agree that the molecular weight of resin is critical to the penetration of resin into the wood cell wall, and thereby accounts for variation of wood dimensional stability (Ryu et al. 1993; Imamura et al. 1998). Resin of low molecular weight can penetrate the wood cell wall more easily, while resin of high molecular weight can only seep into the lumen of wood and therefore yields no gain in dimensional stability of wood (Furunot and Goto 1979; Imamura H et al. 1983; Kajitah and Imamura 1991). PMF co-condensed resin, as a type of resin with low molecular weight, can penetrate into the tracheid, lumen, and cell wall of poplar wood to enlarge the interval among filaments and microfilaments. Meanwhile, due to the numerous hydroxyl groups in diatomite and PMF co-condensed resin, the poplar wood bonds firmly with the diatomite and resin to strengthen the its cell cavities and tracheids. Additionally, the resin blocks the water-exchange channel of wood, decreasing the water absorption and inflation of poplar to some extent, thus enhancing the dimensional stability of specimens (Yu et al. 2011).

The dimensional stability of specimen 2 and specimen 3 was better than specimen 1 (Fig. 3a). Moreover, the bulking effect of specimen 2 and specimen 3 was much weaker than specimen 1 (Fig. 3b). This demonstrated that the presence of diatomite not only strengthened dimensional stability, but also restrained volume expansion. This was because the presence of diatomite enhanced the resin mechanical strength, and played a supporting role on the wood surface. When diatomite was added to the resin, hydroxyl in the resin increased, strengthening the chemical combination with wood. Thus, the dimensional stability of wood was strengthened and the variation in size was reduced. There was, however, no significant difference between specimen 2 and specimen 3, which suggests that the accretion of 3-aminopropyl (diethoxy) methylsilane had no obvious effect on the improvement of the wood dimensional stability.

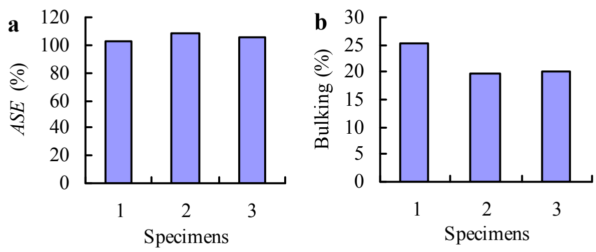

Fig. 3 Dimensional stability (expressed as ASE) and bulking effect of poplar specimen due to the modification with (1) PMF, (2) PMFD1, or (3) PMFD2

Leaching effect

There was a leaching effect on the specimens treated with PMF, PMFD1 or PMFD2, which we attributed to the solubility of PMF co-condensed resin in water (Fig. 4). Song (2008) reported that water and PMF co-condensed resin could be mixed at ratios as high as 1.2 : 1. In our experiment, the curing method for resin in specimens was atmospheric heat treatment only, possibly result-

ing in incomplete curing of the PMF co-condensed resin. Additionally, many bubbles and micro holes (filled with solvent, water and curing product) were generated within the specimen due to the lack of moulding pressure, thus increasing the specific surface area of specimens. Afterwards the uncured resin and soluble small molecules in specimens that were produced after the curing process were dissolved into the water, thus causing the weight loss of specimens. Specimen 3 has the higher leaching rate than specimen 2, and the leaching rate of specimen 1 was the lowest (Fig. 4). This was because the coupling agent improved the distribution of diatomite in resin and more diatomite was deposited and permeated into specimen 3 with PMF co-condensed resin. This increased the specific surface area of poplar, increasing the chance to contact with water, thus enlarging the leaching rate of specimen 3.

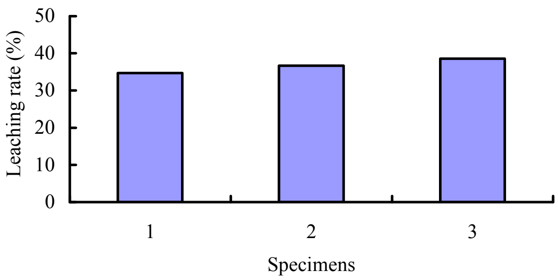

Fig. 4 Leaching effect of poplar specimen due to the modification with (1) PMF, (2) PMFD1, or (3) PMFD2

Water-repellent effectiveness (WRE)

In Fig. 5, the water-repellent effectiveness of all modified specimens increased substantially. Specimen 3 displayed the best WRE throughout the period of immersion in water. Explanations for these results are: (1) The cell lumens of poplar wood after treatment were filled by the diatomite and PMF co-condensed resin, blocking the water-exchange channels of wood and limiting moisture absorption by specimens; (2) Many water adsorption points on wood cell walls were substituted by the groups of modifiers after treatment, which reduced the hydrophilic groups of specimens (Shi et al. 2006); and (3) 3-aminopropyl (diethoxy) methylsilane promoted the combination of resin and diatomite with wood.

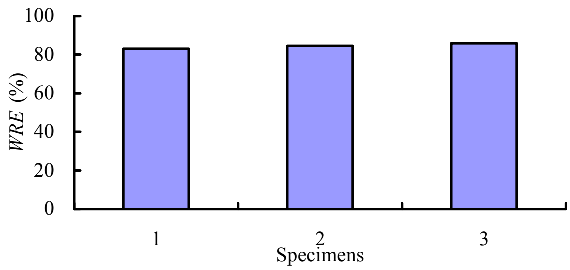

Fig. 5 WRE of poplar specimen due to the modification with (1) PMF, (2) PMFD1, or (3) PMFD2

Antiflaming effect

The oxygen index of treated specimens increased except for specimen 4, which suggests that the antiflaming effect of all modified samples was improved significantly (Fig. 6). This is because the dissociative melamine reserved in PMF co-condensed resin played a positive role in the antiflaming effect of modified specimens. After the thermal decomposition of melamine, the incombustible gases CO_2, NH_3, N_2 and H_2O were released. Correspondingly, the percentage of flammable gas generated during burning of specimens in air was reduced. Meanwhile, the incombustible gas absorbed part of the heat so that the temperature of treated specimens was lower. In addition, the generation of N_2 captured free radicals, restrained polymer chain reactions and prevented burning. Except for the dissociative melamine, the resin contained many nitrogenous elements that could also greatly enhance the flame retardancy of poplar. There were, howeveer, no significant differences between the three oxygen indices, suggesting that the presence of diatomite and the coupling agent had no effect on wood antiflaming (Fig. 6).

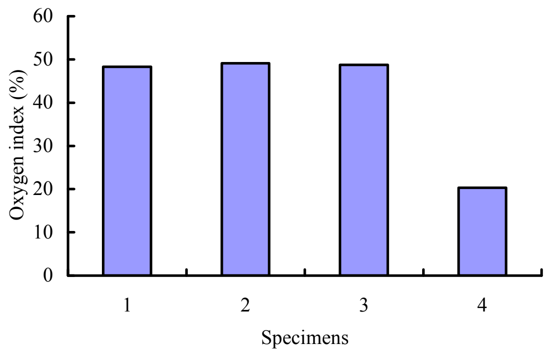

Fig. 6 Oxygen index of poplar specimen due to the modification with (1) PMF, (2) PMFD1, (3) PMFD2, and (4) unmodified poplar wood

Conclusion

The optimal ratio of diatomite dispersed into the PMF co-condensed resin was 0.2%. Composite wood was fabricated from poplar wood by using PMF co-condensed resin, diatomite and 3-aminopropyl (diethoxy) methylsilane. After the impregnation of PMF co-condensed resin and diatomite into the wood, many significant improvements of wood properties were observed, including percent weight gains greater than 150%, anti-swelling efficiency greater than 100%, water-repellent effectiveness increasing by more than 80%, and antiflaming effect increasing by over 48%. The presence of 3-aminopropyl (diethoxy) methylsilane played an important role in further promoting weight increase and water-repellent effectiveness but its effect on all tested wood properties was not marked.

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